Electrochemical Corrosion in Thin Film PV Modules

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ABSTRACT

We have observed that electrochemical corrosion can occur in thin-film photovoltaic (PV) modules that are fabricated on tin oxide coated glass and that operate at high voltages and at elevated temperatures in a humid climate. The current study shows that this corrosion is associated with a delamination of the tin oxide from the glass, which is caused by the accumulation of sodium near the interface between the tin oxide and the glass and by the ingression of moisture into the PV module from the edges.

1. Introduction

Electrochemical corrosion has sometimes been observed in the field for thin-film PV modules fabricated on glass substrates coated with tin oxide [1]. The corrosion usually started at the bottom edge of the PV module frame and appeared to be associated with an incursion of moisture into the module. The corrosion also depended on the voltage applied to the module and involved a complete removal or delamination of the cell structure from the glass surface. This electrochemical corrosion could be minimized by using plastic frames, improving the module edge seals and by using weep holes in the frames to avoid the accumulation of standing water. It was also found that the corrosion could be inhibited by setting up the PV system so that the front contact (the tin oxide) was biased positively with respect to ground [2].

However, electrochemical corrosion effects have been observed on occasion in both amorphous silicon (a-Si) and cadmium telluride (CdTe) PV modules in recent years, especially in modules or arrays that operate at high voltages and at elevated temperatures. In the current work, a number of experiments were performed to identify the root causes of electrochemical corrosion in thin-film PV modules fabricated on glass substrates with different types of transparent conductive oxides.

2. Experimental Details

Most of the experiments in the current study were performed on BP Solar a-Si/a-SiGe tandem PV modules fabricated on tin oxide coated glass and encapsulated with another sheet of glass using EVA (ethylene vinyl acetate) [3]. Some tests were also performed on BP Solar CdTe PV modules fabricated on tin oxide coated glass with a similar encapsulation process. In addition, experiments were performed on samples or coupons, which were made by cutting a 15 cm x 30 cm section out of an a-Si/a-SiGe tandem plate and then encapsulating the coupons in the same manner as the PV modules.

Accelerated corrosion tests were performed on PV modules by applying a forward bias of 70 V for 125 hours at 85°C, 85% relative humidity. Accelerated corrosion tests were performed on coupons by applying a bias of – 100 V to the tin oxide while immersed in a hot salt-water bath. The outer border region of the PV modules and the bottom region of the coupons were identical with a wide isolation strip (WIS) or region (~ 8 mm wide) formed by removing all the devices layers (including the tin oxide) with an abrasion wheel. The device layers were also removed from strips (~ 25 mm wide) along each side of the coupon by sandblasting, and a thin metal foil electrode was attached to the back aluminum contact of the tandem device structure (see Fig. 1). The coupons were encapsulated to another piece of glass using EVA, and a sealant containing a desiccant was applied to the two outer edges of the coupons.

The coupons were partially immersed in a salt-water bath at an elevated temperature (generally 85°C), and –100 V was applied to the foil electrode at the top of the coupon. In a typical experiment, 6 to 12 coupons were placed in the bath at one time, and the total corroded area of each coupon was measured as a function of time. A number of experiments were performed using different glass cleaning procedures, different glass adhesion promoters (in conjunction with EVA as an encapsulant), different encapsulants and different types of transparent conductive oxides (TCO's).

The TCO coatings were characterized using several techniques. A Taber Linear Abraser was used to measure the hardness or abrasion resistance of the oxide layers. Atomic Force Microscopy (AFM) was used to characterize the topography of the TCO's, which was generally textured to enhance light trapping in thin-film solar cell, and X-ray Diffraction (XRD) was used to look at the orientation of the transparent metal oxide crystallites.

3. Experimental Results

The corrosion observed in the coupons always started at the bottom edge and proceeded upward with increasing exposure time to the hot salt-water bath. For coupons biased at –100 V in a salt-water bath at 85°C, a corroded region of several cm^2 (~ 1 – 2 % of the immersed coupon area) was typically evident near the bottom edge of the coupon after 22 hours of exposure. For both coupons and PV modules the corrosion was found to accelerate with increasing negative bias on the tin oxide contact, and no corrosion was observed in any of the tests at zero bias. The corrosion was also observed in coupons made only with a tin oxide layer (no amorphous silicon layers). Disassembling the encapsulated coupons after the bias

treatment showed that the corrosion involved a delamination of the tin oxide from the glass surface.
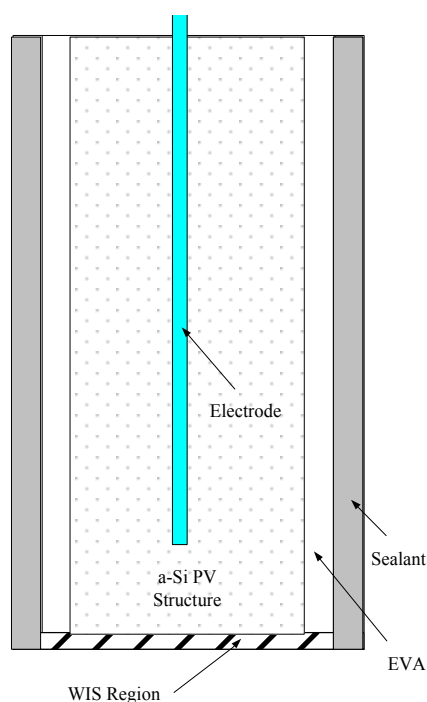

Figure 1. A schematic diagram of a typical coupon used in the accelerated corrosion tests. (WIS stands for wide isolation strip.)

A number of different cleaning procedures were used to clean the exposed glass surface (the WIS region in Fig. 1) before encapsulation. Also, a number of different adhesion promoters (such as organosilanes) were applied to the exposed glass surface near the bottom edge of the coupons before encapsulation. The amount of corrosion observed in the coupons after bias testing in the hot salt-water bath did not vary significantly with the cleaning procedure or with the different adhesion promoters.

However, the corrosion could be delayed or reduced by increasing the width of the isolation region at the bottom of the coupons (the WIS region in Fig. 1). The corrosion was also reduced by applying the sealant containing a desiccant along the WIS region at the bottom of the coupons. These observations support the hypothesis that moisture ingression from the edges of the modules or coupons plays a key role in the corrosion.

When an extra sheet of glass was laminated to half of the front of the tin oxide coated glass sheet, the corroded area on that side of the coupon was reduced by a factor of ~ 4.7. This observation suggests that sodium ion conduction through the glass may also play a role in the corrosion. To further test this hypothesis, a tin oxide coated glass sheet was ion depleted [4] by applying +110 V to the tin oxide layer at 220°C for 1 hour. (An aluminum film was applied to the other side of the glass for the ion depletion treatment and then removed afterwards with a dilute acid.). In the current experiment, we estimate that the ion depletion

treatment removed all sodium (the most mobile ion) to a depth of ~ 700 Å beneath the tin oxide layer. After 46 hours in the biased hot salt-water bath, there was no evidence of any corrosion indicating that sodium ion transport in the glass is playing a major role in the corrosion.

We first characterized the corrosion observed for coupons made with a commercial tin oxide coated glass for treatments in a hot salt-water bath for various times and temperatures. As shown in Fig. 2, there is a delay before corrosion effects are observed, and this delay time is decreased as the bath temperature is increased with an activation energy of about 1 eV. However, once the corrosion starts, the rate of corrosion does not exhibit a strong temperature dependence.
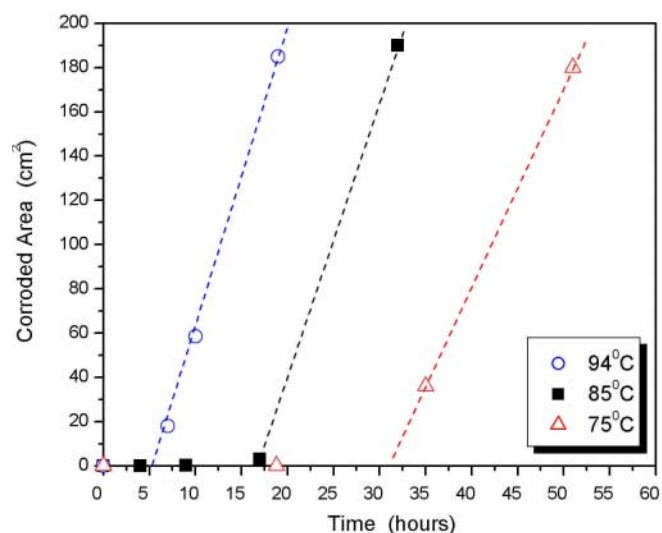

Figure 2. The corroded area vs. time in a hot salt water bath for coupons made with commercial tin oxide coated glass.

We then tested coupons made with tin oxide coated glass supplied by four companies with a total of 17 different deposition conditions and found a wide range of corrosion behavior with the corroded area ranging from 0 to 260 cm^2 after 46 hours at –100 V in a salt-water bath at 85°C. We found that there was a strong correlation of the corrosion resistance with hardness of the tin oxide films as measured by a Taber Linear Abraser before the biased hot salt-water bath test (see Fig. 3). This test involved measuring the resistance of a tin oxide strip as a weighted abrasive head repeatedly traversed the strip perpendicular to the current flow of the resistance meter. The hardness of the tin oxide was quantitatively determined by measuring the number of traverses required to remove the tin oxide locally, which in turn caused the resistance to increase rapidly. The tin oxide films were all on the order of 6000 to 8000 Å thick in the current study. As shown in Fig. 3, the corroded area observed in the biased hot salt-water bath test decreased rapidly to very small values as the hardness of the tin oxide increased. The hardness of the tin oxide is apparently related to the adhesion of the tin oxide to the glass and/or the ability of moisture to penetrate to the interface region between the glass and the tin oxide.
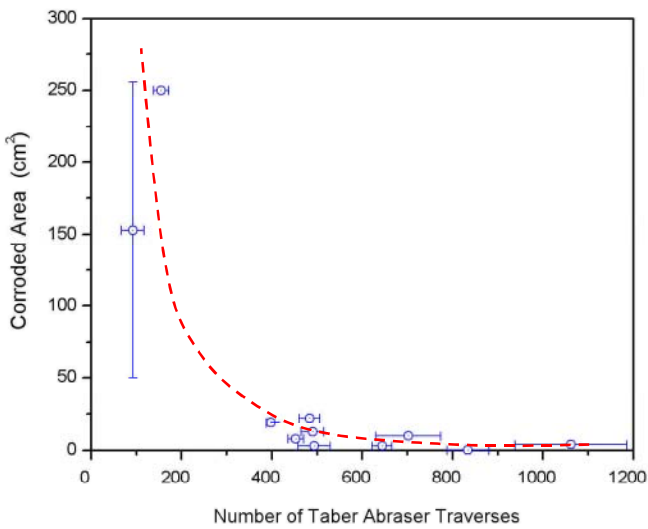
Figure 3. The corroded area in coupons vs. the hardness of the tin oxide as measured by a Taber Liner Abraser.

While Atomic Force Microscopy did not show a significant difference between the topographies of "soft" (~ 90 traverses) and "hard" (~ 450 traverses) tin oxide films, the X-ray diffraction spectra showed that the average orientation of the tin oxide crystallites was different for the same two samples (see Fig. 4). The change in the average crystallite orientation must reflect differences in the nucleation and growth of the tin oxide films, which in turn affects the adhesion of the films to the glass.

A number of large-area (0.8 m^2) tandem PV modules were fabricated using three different tin oxides with Taber abrasion hardness values of ~ 90, ~ 450 and ~ 830. These modules were then subjected to a forward bias of 70 V for 125 hours at 85°C, 85% relative humidity, and the total corroded area was measured for each module. As shown in Fig. 5, the amount of corrosion induced in the modules exhibited a good correlation with that observed in the coupons (where they were biased at –100 V for 46 hours in salt water at 85°C).

The average transmission of coupons made with tin oxide coated glass exhibited a monotonic decrease over the first 100 hours of treatment. The darkening occurred uniformly over the total area of the coupon that was immersed in the salt-water bath and was proportional to the total charge that passed through the glass for treatment times less than 150 hours. The decrease in average transmission at different treatment temperatures was also proportional to the total charge that passed through the glass. We did observe that with increasing treatment time, the darkening was reversed in a growing region originating at the bottom edge of the coupons, apparently due to the penetration of moisture into the coupon. This darkening effect was most evident in the coupons made with "hard" tin oxide since the corrosion was minimal. In addition to the darkening effect, the sheet resistance of the tin oxide in the coupons increased by about an order of magnitude after 200 hours in the biased hot salt-water bath.
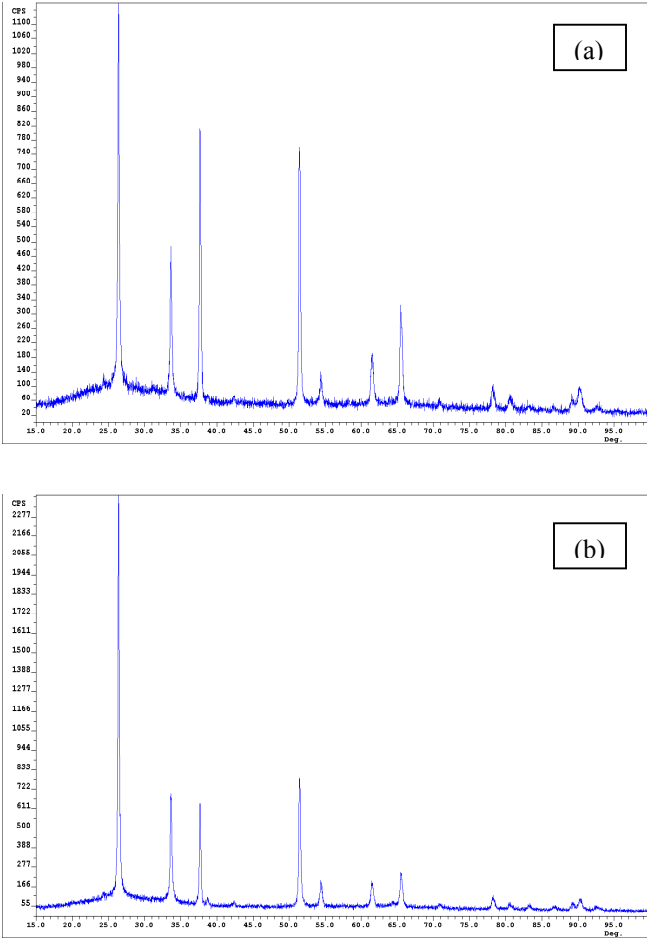

Figure 4. X-ray diffraction spectra for (a) "soft" tin oxide and (b) "hard" tin oxide.
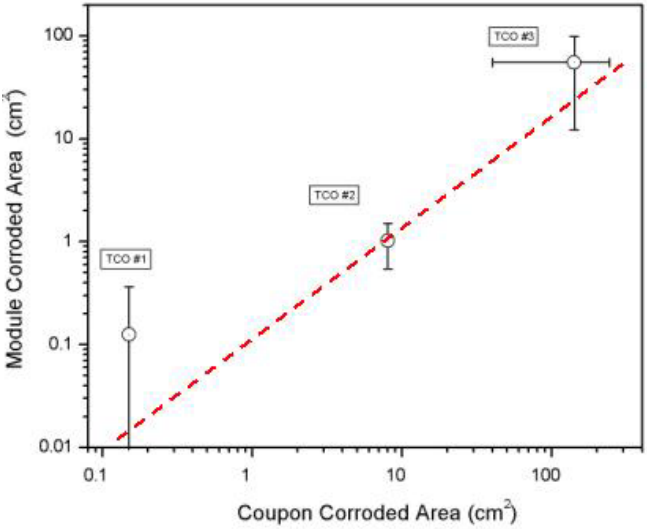

Figure 5. The corroded area observed in modules subjected to a biased damp heat test vs. the corroded area observed in coupons subjected to the biased hot salt-water bath test for three different tin oxide coatings. The film hardness decreased in going from TCO #1 to TCO #3.

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In the case of zinc oxide films made by sputtering and by low-pressure chemical vapor deposition, there was no evidence of corrosion or darkening even after 180 hours in the biased hot salt-water bath at 85°C. In fact, the average transmission of the zinc oxide increased over the entire treatment time. At the same time, the sheet resistance of the zinc oxide increased by about a factor of three after a 180 hour treatment. However, the adherence of the zinc oxide to the glass was weakened by the biased hot salt-water bath treatment since the zinc oxide film tended to adhere to the EVA when the coupons were deliberately broken.

Closer examination of the corrosion-resistant "hard" tin oxide films and the zinc oxide films with an optical microscope revealed evidence of localized blistering. After 270 hours of the biased salt-water bath treatment at 80°C, the "hard" tin oxide films exhibited many small dark circular regions varying from ~ 5 to ~ 50 microns in diameter and other dark regions that were clearly blisters (many containing cracks) with diameters of ~ 10 to ~ 30 microns in diameter. In addition, many of the blisters had joined to form dark blistered segments ~ 100 to 150 microns long. These blisters and dark regions occupied about 30% of the tin oxide film surface area.   Thus, even though the "hard" tin oxide films did not delaminate from the glass substrate, there was evidence of localized blistering for long treatment times in the biased hot salt-water bath.

After 180 hours of the biased hot salt-water bath, the zinc oxide films also exhibited blisters varying from ~ 1 micron to ~ 25 microns in diameter under microscopic examination. However, the blisters were transparent and there was no evidence of any darkened regions as in the case of the tin oxide films. Moreover, the blisters occupied only about 4% of the total zinc oxide surface area.

4. Discussion

The corrosion observed in the current study appears to depend on both sodium ion transport in the glass and on moisture penetration into the module or coupon from the edges. It is well known that sodium ions can move in soda-lime-silicate glass under the influence of an electric field even at relatively low temperatures with an activation energy of ~ 0.8 – 0.9 eV. If the electric field pulls the sodium ions toward the tin oxide, then sodium can accumulate near the interface between the tin oxide and the glass. If moisture ingression occurs, then the sodium can react with the water to form sodium hydroxide and hydrogen. The accumulation of sodium near the glass/tin oxide interface may allow the water to attack the glass and weaken the interfacial bonding (as sodium-rich glasses are soluble in water). Moreover, highly alkaline solutions (pH > 9) such as sodium hydroxide will dissolve silicate glasses rapidly at elevated temperatures (≥ 100°C) [5]. In addition, the generation of hydrogen near the interface may lead to a weakening of interfacial bonds due to the reduction of the tin oxide [6]. The relative durability of the zinc oxide films may be partially due to the fact that atomic hydrogen will not reduce zinc oxide.

The increase in the resistivity of both the tin oxide and zinc oxide films with treatment time in the biased hot salt-

water bath indicates that some sodium is diffusing into the TCO's and changing the optoelectronic properties. However, in the case of the "hard" tin oxide films, some of the sodium appears to be piling up near the interface between the tin oxide and the glass causing both dark regions and blisters, which in turn reduces the average transmission. These sodium-rich regions are bleached when moisture penetrates into the interface region.

In the case of the zinc oxide films, there is no darkening effect indicating that the sodium may move more readily into these films. The increase in average transmission may be associated with an increase in the bandgap of the zinc oxide with increasing sodium content.   Some sodium appears to be accumulating near the interface between the zinc oxide and the glass since the adhesion of the zinc oxide to the glass is reduced and some blistering is evident after a long exposure to the biased hot salt-water bath.

5. Conclusions

In summary, we have shown that thin film PV modules made on glass substrates coated with transparent conductive oxides are susceptible to varying degrees of electrochemical corrosion. PV modules can exhibit performance degradation in the field when subjected to high voltages at elevated temperatures in a humid climate. The current study shows that the tin oxide contacts may delaminate from the glass due to a combination of sodium accumulation near the interface and the ingression of moisture into the PV module from the edges.   The current work shows that these corrosion effects can be minimized by inhibiting moisture ingression, by limiting module or array voltages, by using low-alkali or high resistivity glasses, by increasing the adhesion of the transparent conductive oxide to the glass surface and by using zinc oxide rather than tin oxide as a transparent conductive contact.

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